

CHAPTER 6

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN ADSORPTIVE MEDIA PROCESSES FOR THE REMOVAL OF ARSENIC

Prepared by:
NSF International
789 Dixboro Rd.
Ann Arbor, MI 48105

Copyright 2000 NSF International 40CFR35.6450.

Permission is hereby granted to reproduce all or part of this work, subject to the limitation that users may not sell all or any part of the work and may not create any derivative work therefrom. Contact Drinking Water Systems ETV Pilot Manager at (800) NSF-MARK with any questions regarding authorized or unauthorized uses of this work.

TABLE OF CONTENTS

| | <u>Page</u> |
|---|-------------|
| 1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN..... | 6-5 |
| 2.0 INTRODUCTION..... | 6-5 |
| 2.1 Adsorption Process..... | 6-6 |
| 2.2 Granular Activated Alumina..... | 6-7 |
| 2.3 Other Adsorbents | 6-9 |
| 2.4 Capacity | 6-9 |
| 3.0 GENERAL APPROACH..... | 6-9 |
| 4.0 OVERVIEW OF TASKS | 6-10 |
| 4.1 Task 1: System Integrity Verification Testing | 6-10 |
| 4.2 Task 2: Adsorption Capacity Verification Testing | 6-10 |
| 4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance..... | 6-11 |
| 4.4 Task 4: Data Management | 6-11 |
| 4.5 Task 5: Quality Assurance/Quality Control..... | 6-11 |
| 5.0 TESTING PERIODS..... | 6-11 |
| 6.0 DEFINITIONS | 6-12 |
| 6.1 Adsorb | 6-12 |
| 6.2 Adsorptive Media, Granular | 6-12 |
| 6.3 Adsorptive Media, Powdered | 6-12 |
| 6.4 Bed Volume | 6-12 |
| 6.5 Break-through | 6-12 |
| 6.6 Desorb | 6-12 |
| 6.7 Empty Bed Contact Time (EBCT)..... | 6-12 |
| 6.8 Filtrate | 6-12 |
| 6.9 Ground Water..... | 6-12 |
| 6.10 Regenerate | 6-12 |
| 6.11 Supernatant | 6-12 |
| 6.12 Surface Water..... | 6-12 |
| 6.13 Treatment..... | 6-12 |
| 6.14 Treatment Band..... | 6-12 |
| 6.15 Treatment Bed..... | 6-12 |
| 7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING..... | 6-13 |
| 7.1 Introduction..... | 6-13 |
| 7.2 Experimental Objectives..... | 6-13 |
| 7.3 Work Plan | 6-13 |
| 7.3.1 Spiked Arsenic (Optional)..... | 6-14 |

TABLE OF CONTENTS (continued)

| | <u>Page</u> |
|--|-------------|
| 7.4 Analytical Schedule..... | 6-14 |
| 7.5 Evaluation Criteria and Minimum Requirements | 6-15 |
| 8.0 TASK 2: ADSORPTION CAPACITY VERIFICATION TESTING | 6-15 |
| 8.1 Introduction..... | 6-15 |
| 8.2 Experimental Objectives..... | 6-17 |
| 8.3 Work Plan | 6-18 |
| 8.3.1 Package Plant Operation | 6-18 |
| 8.3.2 RSSCT Operation (Optional) | 6-18 |
| 8.4 Analytical Schedule..... | 6-19 |
| 8.5 Evaluation Criteria and Minimum Reporting Requirements..... | 6-19 |
| 8.5.1 Record of Arsenic Removal | 6-19 |
| 8.5.2 Process Control..... | 6-20 |
| 9.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE | 6-20 |
| 9.1 Introduction..... | 6-20 |
| 9.2 Experimental Objectives..... | 6-20 |
| 9.3 Work Plan | 6-20 |
| 9.4 Schedule..... | 6-21 |
| 9.5 Evaluation Criteria | 6-21 |
| 10.0 TASK 4: DATA MANAGEMENT | 6-21 |
| 10.1 Introduction..... | 6-21 |
| 10.2 Experimental Objectives..... | 6-21 |
| 10.3 Work Plan | 6-21 |
| 11.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) | 6-22 |
| 11.1 Introduction..... | 6-22 |
| 11.2 Experimental Objectives..... | 6-23 |
| 11.3 Work Plan | 6-23 |
| 11.3.1 Daily QA/QC Verifications..... | 6-23 |
| 11.3.2 Weekly QA/QC Verifications | 6-23 |
| 11.4 Analytical Methods | 6-24 |
| 11.4.1 Arsenic..... | 6-24 |
| 11.4.2 pH..... | 6-24 |
| 11.4.3 Alkalinity | 6-24 |
| 11.4.4 Fluoride..... | 6-24 |
| 11.4.5 Chloride | 6-24 |
| 11.4.7 Silica..... | 6-24 |
| 11.4.8 Aluminum | 6-24 |
| 11.4.9 Sodium..... | 6-24 |
| 11.4.10 Calcium..... | 6-25 |

TABLE OF CONTENTS (continued)

| | <u>Page</u> |
|---|-------------|
| 11.4.11 Hardness | 6-25 |
| 11.4.12 Magnesium..... | 6-25 |
| 11.4.13 Iron | 6-25 |
| 11.4.14 Manganese | 6-25 |
| 11.4.15 Turbidity | 6-25 |
| 11.4.16 Temperature | 6-25 |
| 11.5 Chemical Samples Shipped Off-Site for Analyses | 6-25 |
| 11.6 Tests and Data Specific to Adsorptive Media Type Evaluated | 6-25 |
| 12.0 OPERATIONS & MAINTENANCE..... | 6-26 |
| 12.1 Operation | 6-26 |
| 12.2 Maintenance..... | 6-27 |
| 13.0 REFERENCES..... | 6-27 |

TABLES

| | <u>Page</u> |
|--|-------------|
| Table 1. Schedule for observing and recording package plant operating and performance data | 6-29 |
| Table 2. System Integrity Verification Test Chemical Consumption Data Report | 6-30 |
| Table 3. Required water quality analyses and minimum sample frequencies for System Integrity Verification Testing..... | 6-31 |
| Table 4. Tests and data specific to adsorptive media type evaluated..... | 6-32 |
| Table 5. Schedule for observing and recording RSSCT operating and performance data..... | 6-32 |
| Table 6. Required water quality analyses and minimum sample frequencies for Adsorption Capacity Verification Testing | 6-33 |
| Table 7. Adsorption Capacity Verification Data Report..... | 6-34 |

APPENDICES

| | |
|------------|---|
| Appendix A | Arsenic Speciation Method Developed by Battelle for EPA |
|------------|---|

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the NSF Equipment Verification Testing Plan for evaluation of water treatment equipment for arsenic removal utilizing the adsorptive media process. This Testing Plan is to be used as a guide in the development of Field Operations Document (FOD) procedures for testing adsorptive media equipment, within the structure provided by the NSF Protocol Document, "Protocol for Equipment Verification Testing for Arsenic Removal." This Equipment Verification Testing Plan is applicable only to granular adsorptive media processes that use activated alumina, or other material that attracts arsenic ions to adsorption sites, with or without pH adjustment in fixed or moving packed beds. Powdered adsorptive media may also be effectively utilized in combination with chemicals in Coagulation and Filtration Arsenic Removal Processes. Since performance of powdered adsorptive media is to be included in that equipment category it is not included in this Testing Plan.

In order to participate in the equipment verification process for adsorptive media, the equipment Manufacturer and their designated Field Testing Organization (FTO) shall employ the procedures and methods described in this test plan and in the referenced NSF Protocol Document as guidelines for the development of the FOD. The procedures shall generally follow those Tasks related to Verification Testing that are outlined herein, with changes and modification made for adaptations to specific equipment. At a minimum, the format of the procedures written in the FOD for each Task should consist of the following sections:

- a) Introduction
- b) Objectives
- c) Work Plan
- d) Analytical Schedule
- e) Evaluation Criteria

Each FOD shall include Tasks 1 through 5. An overview of Tasks 1 through 5 is provided in Section 4.0 of this Testing Plan.

2.0 INTRODUCTION

This Equipment Verification Testing Plan is applicable to the testing of package and modular water treatment equipment utilizing an adsorptive media process which may include a pretreatment pH adjustment step. Verification Testing shall evaluate performance of the equipment under at least one feed water quality condition. Waters containing naturally occurring arsenic are preferable to synthetic water "spiked" with arsenic. Use of feed water artificially spiked with arsenic, a product of a non-standard method, might provide inaccurate performance data which will not reflect performance data acquired with use of natural water. Verification Tests will be performed for relatively short time intervals during time periods when the source water or feed water quality is appropriate for testing the full range of water quality conditions that need to be evaluated.

Adsorption can be an effective treatment technique for removing arsenic prior to disinfection application. Adsorptive media processes are operated as filters usually containing a 28x48 US Standard Mesh size. Typical empty-bed contact times (EBCTs) are 5 to 10 minutes. Arsenic removal is typically greater than 99 percent at the beginning of adsorptive media vessel operation for EBCTs greater than 5 minutes. Over time, effluent concentrations increase, yielding a characteristic breakthrough curve that is unique to the water source, pretreatment conditions, EBCT, and type of adsorptive media used. Thus, the adsorptive media vessel run time for a given treated water criterion can be determined from the appropriate break-through curve. Once effluent criteria are exceeded, the adsorptive media must be regenerated or replaced with new adsorptive media.

This Verification Testing Plan is not intended to be used for the evaluation of ability of adsorptive media to serve as a particulate matter (turbidity) filter. The NSF Equipment Verification Testing Plan for Coagulation and Filtration should be used in conjunction with this Testing Plan when verification of particulate matter filtration performance is required.

2.1 Adsorption Process

The adsorption process is the physical attraction of the ion to be adsorbed to the surface of the adsorbent material. The adsorbed ion (adsorbate) gathers on to the surface of the adsorbent. The process is sensitive to the concentration of the adsorbate, the surface area of the adsorbent, the physical characteristics of both the adsorbent and/or the adsorbate, competing ions, time, and flow characteristics of the medium conducting the adsorbate into the treatment bed of adsorbent. In this case arsenic is the adsorbate. Arsenic occurs in water in two valence states (As III and As V.) The valence state can be modified by oxidation and reduction processes. The toxicology of arsenic varies depending upon its concentration and valence. Since arsenic valence can change while in aqueous solution, the objective of arsenic removal treatment is to remove all of the arsenic regardless of valence. The higher the raw water arsenic concentration the higher the adsorptive driving force and the higher the arsenic capacity of the adsorptive media. The adsorptive capacity of the treatment media is also a function of the surface area (adsorption sites) and the access to those sites. An adsorptive media's surface area is a function of its porosity. An adsorptive treatment media contains an extensive network of fine (small diameter) pores which extend throughout the body of a grain of media. The adsorptive attraction force is a function of the pore size, the ion size, the pH and other physical conditions. The arsenic ion requires time to migrate into a pore within the grain of the adsorbent. As the surface area of each adsorbent grain becomes saturated with arsenic ions, the time required for additional adsorption becomes longer. The adsorptive media is normally in a packed bed. The water to be treated flows in one direction through the treatment bed (normally downflow). The treatment media is normally contained in a pressure vessel. Gravity flow is feasible; but, if pH adjustment is employed, gravity flow is not as effective because in gravity flow the pressure required to retain the CO₂ in solution does not exist. Therefore, the free CO₂ is released resulting in the pH rising to higher than the desired level. As the feed water flows through the adsorptive media, the arsenic ions are adsorbed onto the available adsorption sites. As the adsorption sites are being occupied, the arsenic ion concentration decreases in the water. As the water flows through the bed its arsenic concentration decreases until no longer detectable. The water continues to flow through the media until it exits the treatment vessel as treated water. As the feed water continues to flow

through the treatment media the media which first contacts the feed water becomes saturated with arsenic ions. A treatment band then progresses through the treatment bed until breakthrough occurs. At that point, traces of arsenic appear in the treated water. As flow continues the treatment band progresses through the treatment media until the media is saturated; the arsenic concentration in the treated water is then the same as that in the feed water. Since the arsenic concentration in the treated water is the regulated contaminant, the arsenic concentration must be controlled to comply with the regulated maximum containment level (MCL). There are various methods of sequencing multiple treatment beds (parallel and/or series arrangements) which allow the entire (or almost the entire) adsorptive media capacity to be utilized. When the adsorptive media becomes saturated with arsenic ions it is removed from service for regeneration or disposal. Normally the economic feasibility of the adsorptive process requires reuse of the treatment media. This is accomplished by means of chemical regeneration requiring adjustment of pH (or other methods) to a level at which adsorptive conditions no longer exist. At those pH levels the adsorptive treatment media desorbs the adsorbate. The arsenic is released and flushed from the adsorptive media as a high concentration arsenic wastewater. Upon completion of regeneration, the pH of the treatment media is to be adjusted back to the treatment pH at which point the media is reused for a subsequent treatment cycle. During a regeneration, some adsorptive media may be consumed (attrition); if that occurs, replacement adsorptive media is to be added to the treatment bed. In small treatment systems and/or in treatment systems in which the arsenic concentration in the feed water is not excessively higher than the MCL, economic feasibility might dictate replacement of spent media in lieu of regeneration.

Historically the adsorptive media that has demonstrated the most cost effective, reliable performance has been granular activated alumina. Other adsorptive media such as bone char, and synthetic bone char (tri-calcium phosphate) have also been employed; but have not performed as effectively as activated alumina. New adsorbents are currently being developed and can be included within this Protocol for Equipment Verification Testing.

2.2 Granular Activated Alumina

Granular activated alumina has been successfully implemented as an adsorptive treatment media for the selective removal of arsenic from potable water. Although this adsorbent removes other inorganic and organic contaminants from water, it prefers arsenic. The activated alumina process is pH sensitive. pH 5.5 has been determined to be the optimum level at which the activated alumina has the greatest capacity for arsenic. Treated water pH must be readjusted to a desired level. As the pH deviates higher or lower from the optimum level, the capacity for arsenic reduces until it reaches zero. At those high and low pH levels, regeneration of the media can take place. The activated alumina adsorptive process with pH adjustment removes all arsenic regardless of valence. The adsorptive capacity of the media is also sensitive to the arsenic concentration in the feed water. The higher the feed water arsenic concentration the higher the arsenic capacity of the activated alumina. Ions that are also adsorbed by the treatment media, such as fluoride, selenium, silica, etc., that might occur in combination with arsenic in a specific feed water might compete with the arsenic for adsorption sites on the surface of the adsorptive treatment media. Depending upon the pH of the treated water and the concentration of the competing ions, the adsorptive capacity of the treatment media for arsenic might be affected. During a treatment run at the 5.5 pH arsenic continues to be adsorbed by the activated

alumina long after adsorption of the competing ions has terminated; the competing ions might desorb as arsenic continues to adsorb.

Without pH adjustment the arsenic capacity of the activated alumina adsorption process might be reduced by more than 95%. Thereby, without pH adjustment the economic feasibility of this arsenic removal method is significantly diminished.

The main advantages of the arsenic removal process using activated alumina with pH adjustment are as follows:

- a) The process is feasible. (Adjust feed water pH, flow through activated alumina adsorptive media, readjust treated water pH to desired level.)
- b) The process removes arsenic below 5 g/l regardless of valence. Total arsenic can be removed by means of two treatment beds in series. Utilizing this concept, arsenic breakthrough can be prevented.
- c) At the optimum treatment pH the process removes arsenic preferentially to all known competing adsorbates. Competing ions do not create desorption spikes.
- d) Wastewater disposal is feasible. Wastewater quantity is a very low percentage of production potable water. High pH wastewater is neutralized to precipitate a high arsenic concentration sludge that is efficiently dewatered. The wastewater supernatant and filtrate may contain arsenic levels lower than that in the feed water. Therefore several simple liquid wastewater disposal methods including discharge to local sewers, landscape irrigation, cooling tower makeup, industrial process makeup water, surface discharge, percolation, etc. are available. The dewatered solids pass EPA criteria for non-toxic/non-hazardous solid material; therefore, sanitary landfill disposal is an option.

Potential problems with the arsenic removal process using activated alumina with pH adjustment are as follows:

- a) Corrosive chemicals (acid and caustic) are required for treatment and/or regeneration. Handling and storage of these chemicals requires care in treatment plant chemical storage subsystem design and operator training. If exhausted treatment media is removed and replaced in lieu of regeneration, the requirement for caustic might be eliminated.
- b) High iron in groundwater or surface water might require pretreatment for removal to avoid excessive requirement for backwash of adsorptive media.
- c) Turbidity in groundwater or surface water might require pretreatment for removal to avoid excessive requirement for backwash of adsorptive media.
- d) Extremely high feed water arsenic level (greater than 0.500 mg/L) might require a pretreatment such as chemical precipitation/ sedimentation/ filtration to provide a more economic treatment system concept.

- e) Other toxic contaminants (inorganic and/or organic) in combination with arsenic might require additional pretreatment and/or post treatment.
- f) High levels of aluminum (greater than 0.1 mg/L) can be present in the treated water for a short period following placement of new media or regeneration of spent media. The operator is required to monitor the aluminum level during the neutralization phase of a regeneration until the soluble aluminum reduces to an acceptable level.
- g) Prechlorination has degraded performance of granular activated alumina. Therefore UV disinfection is suggested as pretreatment for surface feed waters.

2.3 Other Adsorbents

Other adsorbents to be included in this Protocol for Equipment Verification Testing category are:

- a) Granular activated alumina with surface treatment
- b) Granular activated alumina with pretreatment of feed water other than pH adjustment.
- c) Granular bone char (or synthetic bone char)
- d) Granular activated carbon with surface treatment
- e) Other adsorbent materials

2.4 Capacity

Capacities and performance of different adsorptive media do vary. Some adsorptive media may be capable of regeneration while others may not. Those adsorptive media that have regeneration capability also may vary in performance during subsequent treatment runs. The arsenic removal capacity diminishes until it is determined that adsorptive media replacement is required. Other adsorptive media experiences attrition during each regeneration requiring addition of makeup adsorptive media prior to commencement of the next arsenic removal treatment run. The latter type of adsorptive media may not experience reduction of arsenic removal capacity during subsequent treatment runs.

3.0 GENERAL APPROACH

This Verification Testing Plan is directed to the completion of two main tasks: System Integrity Verification Testing and Adsorption Capacity Verification Testing. System Integrity Verification Testing is a two-week field operation of the package plant with monitoring to ensure the system is functional and to identify any major systemic problems such as channeling, insufficient media, excessive headloss buildup, etc. This Testing Plan includes sampling and monitoring requirements for System Integrity Verification Testing. Adsorption Capacity Verification Testing is intended to evaluate the ability of the type of adsorptive media and contact time utilized to remove arsenic to the level claimed by the manufacturer. An example of a performance claim statement that may be included in an FOD is: "This package plant, when operated at an adsorption media EBCT of 5 minutes or more, is capable of achieving an effluent arsenic concentration in compliance with the MCL for at least 50 days for influent arsenic

concentrations up to 0.120 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V).”

Testing shall be conducted by an NSF-qualified FTO that is selected by the Manufacturer. Water quality analytical work to be completed as part of this NSF Equipment Verification Testing Plan shall be contracted with a laboratory that is certified, accredited or approved by a State, a third-party organization (i.e., NSF), or the U.S. EPA.

The influent water quality chosen for Adsorption Capacity Verification Testing should reflect the claims that the Manufacturer intends to make on the package plant performance. Multiple claims made on the ability of a package plant to treat a variety of influent water quality conditions must be supported by Adsorption Capacity Verification Testing performed under conditions representative of this range of water quality. Adsorption Capacity Verification Testing must be conducted at least once using the package plant. Subsequent testing may be performed in the field using the package plant or in a laboratory using the rapid small-scale column test (RSSCT), a rapid bench-scale adsorptive media test. The RSSCT shall be designed to simulate the EBCT of the package plant and shall use a representative sample of the adsorptive media used in the package plant.

The manufacturer shall stipulate which pretreatment processes are necessary prior to the adsorptive media. The recommended pretreatment processes shall then be employed as pretreatment during Equipment Verification Testing. Adsorptive media performance will be evaluated based on influent water quality, sampled after any pretreatment processes. If Adsorption Capacity Verification Testing is conducted using RSSCTs, any Manufacturer recommended pretreatment process must be simulated prior to the RSSCT. Alternatively, the water used as influent to the RSSCT may be sampled from a package plant or full-scale treatment plant employing representative the recommended pretreatment process.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the tasks included in the adsorptive media Verification Testing Plan.

4.1 Task 1: System Integrity Verification Testing

The objectives of this task are to demonstrate that the package plant is (1) able to initially produce a finished water of acceptable quality, and (2) able to reliably operate under field conditions. The package plant is operated, monitored, and sampled for approximately two weeks.

4.2 Task 2: Adsorption Capacity Verification Testing

The objectives of this task are to evaluate the ability of the adsorptive media package plant to meet the water quality objectives specified by the Manufacturer. The performance of the adsorptive media package is a function of the type of adsorptive media used and the feed water

quality. Task 2 Adsorption Capacity Verification Testing must be performed at least once using the package plant and may be repeated, as necessary, using different water sources to verify the ability of the package plant to meet multiple treated water quality objectives stated by the Manufacturer. If Task 2 is repeated, testing may involve the package plant or the optional RSSCT may be utilized for Adsorption Capacity Verification Testing. Adsorptive media influent and effluent analyses performed include arsenic, pH and other ions that are identified in the feed water (see Table 6). The duration of testing will depend on treatment goals supplied by the Manufacturer.

4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

During each day of Verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. The volumetric flow rate through adsorptive media vessels is a critical parameter, and shall be frequently monitored, recorded, and adjusted if necessary. Adsorptive media performance is affected by the EBCT, which is a function of the volumetric flow rate through the adsorptive media vessel.

4.4 Task 4: Data Management

This task will establish effective field protocol for data management at the field operations site and for data transmission between the Field Testing Organization and the NSF.

4.5 Task 5: Quality Assurance/Quality Control

The objective of this task is to ensure accurate measurement of operational and water quality parameters during Verification testing.

5.0 TESTING PERIODS

Task 1, System Integrity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5 in a two-week period, not including mobilization and start-up. Task 2, Adsorption Capacity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5. The duration of Task 2 is dependent on the run time or volume of water required to verify Manufacturer's treatment claims, the source water quality, and whether testing is conducted using a package plant or the optional rapid bench-scale test (RSSCT). The RSSCT is described later in paragraph 8.1 of this Testing Plan. The expected duration of Adsorption Capacity Verification Testing may range from 1 to 6 months. (NOTE: This was removed here because it is stated later in the section describing RSSCT.)

6.0 DEFINITIONS

- 6.1 Adsorb:** To adhere on a surface in a condensed layer.
- 6.2 Adsorptive Media, Granular:** Particles retained on a 100 mesh screen that have ability to adsorb. During the treatment process these materials are contained in a treatment vessel.
- 6.3 Adsorptive Media, Powdered:** Particles that pass through a 100 mesh screen that have ability to adsorb. During the treatment process these particles are added into and mixed with the water to be treated. The particles are removed from the treated water by sedimentation and/or filtration.
- 6.4 Bed Volume:** The volume of adsorptive media including voids between particles contained in a treatment vessel.
- 6.5 Break-through:** The point in adsorptive media run time when the effluent arsenic concentration reaches a predetermined value, such as the detection limit, the MCL, some fraction of the MCL, etc.
- 6.6 Desorb:** To remove an adsorbate from an adsorptive media surface.
- 6.7 Empty Bed Contact Time (EBCT):** The volume of the media divided by the flow rate. For example, the time (EBCT) required for feed water flowing at 150 gpm through an adsorptive treatment media volume of 100 ft³ (750 gallons) is 5 minutes.
- 6.8 Filtrate:** Liquid that has passed through a filter.
- 6.9 Ground Water:** Water located below grade which is not under the influence of surface water. The source of water in wells and springs.
- 6.10 Regenerate:** To renew or restore treatment capacity to adsorptive media.
- 6.11 Supernatant:** Liquid above a sludge layer.
- 6.12 Surface Water:** All water which is open to the atmosphere and subject to surface runoff. For purpose of this document, surface water includes lakes, reservoirs, canals, rivers, streams, and ground water under the influence of surface water.
- 6.13 Treatment:** To subject to some agent or action in order to bring about a particular result.
- 6.14 Treatment Band:** The portion of a bed of adsorptive media in which treatment takes place.
- 6.15 Treatment Bed:** The space occupied by the adsorptive media.

7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING

7.1 Introduction

This task will evaluate the short-term ability of the package plant to produce water of acceptable quality. This task is not designed to evaluate the long-term ability of the package plant to remove arsenic.

7.2 Experimental Objectives

The objectives of this task are to demonstrate that the package plant is (1) able to produce a treated water in compliance with the MCL, and (2) able to reliably operate under field conditions.

7.3 Work Plan

The Manufacturer and their designated FTO shall specify in the FOD the operating conditions to be evaluated during verification testing and shall supply written procedures on the operation and maintenance of the treatment system. To complete the System Integrity Test, the treatment system shall be operated continuously for a minimum of 320 hours (13 full days plus one 8-hour work shift) unless the minimum duration is reduced at the discretion of the FTO. For adsorptive media vessels operated as post-filter adsorbers, the media filters on-line upstream of the adsorptive media vessels shall be operated from start-up until turbidity break-through or terminal head loss is attained, at which time the media filters shall be backwashed and operation shall resume. System Integrity Verification Testing shall include at least one backwashing event, as determined by turbidity break-through or terminal head loss. Interruptions in the treatment system shall be documented and are allowed only for backwashing events and required equipment maintenance. Since adsorptive media performance is a function of EBCT, which is dependent on the volumetric flow rate, it is critical that verification testing be conducted at a set flow rate that is maintained within 5 percent of the design value.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the Analytical Schedule (see Table 3). Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the FOD.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in TASK 5, Quality Assurance/Quality Control.

7.3.1 Spiked Arsenic (Optional)

If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's removal claim, arsenic spiking may be employed. Spiked arsenic may be used in concentrations sufficient to permit the most-stressed operations for the Manufacturers' equipment, following the recommended guidelines:

- Arsenic spiking shall begin at start-up of the treatment equipment.
- Arsenic feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free.
- To spike arsenic (III), use commercially-prepared arsenic trioxide. (In cold water, at 2°C, the solubility of this chemical is about 1.2 g/100 g water.)
- To spike arsenic (V), use commercially-prepared arsenic pentoxide.
- Feed reservoir for the arsenic spike solution shall be made of chemically inert material (i.e., not reactive or adsorbable to the arsenic).
- The reservoir will be mixed continuously throughout the experiment.
- The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- Use an in-line static mixer to mix this solution into the feedwater.
- Arsenic samples of at least 250 mL shall be collected in bottles prepared for holding such samples.

If testing with Arsenic (III) is contemplated, Manufacturers and Field Testing Organizations need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the package plant. Manufacturers and Field Testing Organizations should also be aware that there are professional opinions that are opposed to arsenic spiking for adsorptive media verification testing.

If arsenic (III) is spiked, then speciation tests shall be conducted to verify that the arsenic (III) is being fed to the treatment system. The application test that was developed by Battelle for the EPA shall be employed (see Appendix A). Also, if the adsorptive media to be tested does not efficiently remove Arsenic (III), the speciation test developed by Battelle shall be employed.

7.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include, at a minimum, system flow rates and head loss or pressure. Operational data monitoring frequencies are described in Table 1. The FTO shall include acceptable values and ranges for all operational parameters monitored. Data organization and recording is important. An example of chemical consumption data recording is illustrated in Table 2.

Water Quality Data Collection. During System Integrity Testing, the adsorptive media feed water quality and adsorptive media treated water quality shall be characterized by analysis of the water quality parameters listed in Table 3. Additional or more frequent analyses may be stipulated at the discretion of the FTO.

The first sampling for each required analyte shall be performed by means of grab samples one day after plant operation start-up, and then by the frequency given. Although many parameters may be analyzed off-site, pH, temperature, and turbidity must be analyzed on-site.

The above water quality parameters are listed to provide State drinking water regulatory agencies with background data on the quality of the feed water being treated and the quality of the treated water. These data are to be collected to enhance the acceptability of the System Integrity Verification Testing to a wide range of drinking water regulatory agencies.

7.5 Evaluation Criteria and Minimum Reporting Requirements

The results of System Integrity Verification Testing shall be evaluated based on arsenic removal. Time series plots shall be generated describing adsorptive media influent and effluent arsenic.

The System Integrity Verification Testing should demonstrate the initial ability of the adsorptive media to remove arsenic concentration below detectable levels in the treated water. Detectable levels of immediate break-through of arsenic are indicative of failure of the treatment system, possibly due to hydraulic channeling, insufficient media, very low adsorptive media capacity, or inappropriate adsorptive media design for the water quality tested. Long term arsenic removal will be evaluated during Task 2 (Adsorption Capacity Verification Testing.)

8.0 TASK 2: ADSORPTION CAPACITY VERIFICATION TESTING

8.1 Introduction

The purpose of Task 1 System Integrity Verification Testing is to quickly and efficiently test the basic ability of the adsorptive media vessel (1) to initially yield a treated water of acceptable water quality and (2) to reliably operate under field conditions. After Task 1 has been performed the long term effectiveness of the treatment system to remove arsenic shall be evaluated by Task 2 Adsorption Capacity Verification Testing. For a tabulation of physical data requirements for the adsorption media being evaluated see Table 4.

The break-through of arsenic for a given water source is characteristic of the treatment system and will depend on design, EBCT, the type of adsorptive media used, and feed water quality. Break-through is highly dependent on the concentration and adsorptive characteristics (isotherm) of the arsenic to be treated by the adsorptive media. Since adsorptive media performance is dependent on feed water quality, the Manufacturer may make multiple claims on the arsenic removal ability of the package plant. To verify these claims, the FTO shall repeat Adsorption Capacity Verification Testing, utilizing multiple water qualities representative of those described in the claims, as described below in the Work Plan.

Adsorption Capacity Verification Testing shall be performed at least once for a package plant, but may be performed multiple times on different water qualities to verify the Manufacturer's claims made on the ability of the package plant to remove arsenic under various feed water quality conditions.

After Task 2 Adsorption Capacity Verification Testing is performed at least once using the package plant, subsequent Adsorption Capacity Verification Testing may be performed either using the package plant or the rapid small-scale column test (RSSCT). The RSSCT is a scaled version of an adsorption media vessel, utilizing a smaller particle size adsorptive media designed with scaling equations that maintain similitude to the full-scale system. A proportional diffusivity approach is used as diffusion to adsorption sites has been shown to be proportional to adsorptive media particle size. Therefore, run times to adsorptive media effluent criteria are shortened by a factor proportional to the ratio of the full-scale adsorptive media particle size to the RSSCT adsorptive media particle size. The main advantage of the RSSCT approach is that run times are shortened to 5-20 percent of full-scale run times. A relatively small amount of water is needed, which can be transported to an off-site laboratory. Furthermore, the RSSCT approach does not require an evaluation of adsorption capacity and kinetics by separate experiments or the use of numerical or analytical models.

The Granular Activated Carbon Precursor Removal Studies section of the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (Treatment Studies Manual) contains guidance regarding RSSCT design, operation, and monitoring. This reference document, though prepared specifically for granular activated carbon (GAC), contains methodology that is adaptable to the application of adsorptive media for the removal of arsenic from potable water by means of the RSSCT. The procedures contained in the Treatment Studies Manual shall be followed when performing RSSCTs, with the following exceptions:

- a) Design of the RSSCT shall be based on the actual EBCT utilized for the adsorptive media in the package plant. The Treatment Studies Manual specifies that RSSCTs be designed with full-scale equivalent EBCTs of 10 and 20 minutes. For verification testing, RSSCTs must be designed based on the package plant adsorptive media vessel EBCT under normal operation conditions.
- b) The RSSCT feed water should ideally be sampled from the package plant after all treatment steps that remove arsenic but prior to the adsorptive media. If water samples are taken from an existing water treatment plant, then all treatment steps performed on and chemicals added to the water sample must be representative of the package treatment plant. If raw water is sampled and batch treated in an off-site laboratory, then the batch treatment must simulate the treatment conditions, chemical dosages, and resulting arsenic removal of the pretreatment steps in the package treatment plant.
- c) Sampling and analytical methods must be performed as described below in the Analytical Schedule section of Adsorption Capacity Verification Testing.

- d) The FTO shall specify a run time criteria for each Adsorption Capacity Verification Testing period. Run time criteria can be based on treated water quality conditions, or set to a specific maximum run time.
- e) Performing quarterly RSSCT sessions to capture seasonal variability for a given water source (as required in the Treatment Studies Manual) is not necessary. However, multiple RSSCT runs on different water sources with varying water qualities may be necessary to verify the Manufacturer's claims made on the ability of the package plant to remove arsenic under a range of water quality conditions.

One drawback of the RSSCT stems from the use of a batch feed water sample: a single RSSCT experiment will not show the effects of long-term seasonal variability that may be captured during a full-scale run. The selection of a representative batch water sample for the RSSCT is extremely important as changes in feed water concentration and adsorbability can lead to misleading results as compared to full-scale results.

It should be noted that the RSSCT is not a standard method for arsenic adsorptive media. Interim, non-standard methods for RSSCT for adsorptive media for the removal of arsenic may be used for ETV verification testing. However, any interim RSSCT for adsorptive media for the removal of arsenic is subject to review by experts and possible subsequent method changes

After initial Adsorption Capacity Verification Testing is performed using the package plant, Adsorption Capacity Verification Testing may be performed either by use of the package plant treatment system, or by RSSCTs designed to simulate the treatment conditions utilized in the package plant. Manufacturers interested in verifying multiple claims based on treatment of varying adsorptive media feed water qualities may find that Adsorption Capacity Verification Testing performed using a series of RSSCTs will decrease the time and effort required to assess system performance for arsenic removal.

8.2 Experimental Objectives

The objectives of this task are to evaluate the ability of the adsorptive media employed in the treatment system to meet the water quality objectives specified by the Manufacturer.

The FTO shall identify in the FOD the treated water quality objectives to be achieved in the statement of performance capabilities of the equipment to be evaluated during verification testing. The statement of performance capabilities prepared by the Manufacturer shall indicate the range of water quality under which the equipment can be challenged while successfully treating the adsorptive media feed water. One example of a statement for demonstration of water treatment capabilities is provided below:

“This package plant, when operated at an adsorption media EBCT of 5 minutes or more, is capable of achieving an effluent arsenic concentration in compliance with the MCL for at least 50 days for influent arsenic concentrations up to 0.120 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V).”

8.3 Work Plan

The FTO shall specify in the FOD run time criteria for each Adsorption Capacity Verification Testing period. Run time criteria can be based on treated water quality conditions, or set to a specific maximum run time. For example, the FTO may specify that the equipment be operated until the treated arsenic concentration reaches 0.050 mg/L. Alternatively, the FTO may specify a maximum run time of 60 days. A combination of treated water quality and maximum run time criteria may also be utilized.

The run time criteria chosen should reflect the claimed treatment capability of the system, based on the adsorptive media feed water quality. Therefore, water sources must be chosen carefully so that water qualities are representative of that upon which the Manufacturer's treatment capabilities are based. Specifically, the measured feed water arsenic concentration during verification testing must average within 10 percent of the amount stated in the Manufacturer's treatment claim. This stipulation ensures that Adsorption Capacity Verification Testing adequately tests the package plant's ability to meet Manufacturer's claims for a given water quality. Multiple Adsorption Capacity Verification Testing periods will be necessary to provide verification testing on multiple treatment capability claims. For example, a minimum of five Adsorption Capacity Verification Testing runs are required to inclusively verify water treatment claims made on water qualities with adsorptive media feed water arsenic concentrations ranging between 0.050 and 0.200 mg/L.

If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's removal claim, arsenic spiking may be employed (refer to procedures outlined in Section 7.3.1).

8.3.1 Package Plant Operation

In assessing package plants, Task 2 Adsorption Capacity Verification Testing may begin simultaneously with Task 1 System Integrity Verification Testing. Subsequent sessions of Task 2 Adsorption Capacity Verification Testing will not require Task 1 System Integrity Verification Testing. The FTO shall specify the operating conditions to be utilized during verification testing and shall supply written procedures on the operation and maintenance of the treatment system.

8.3.2 RSSCT Operation (Optional)

The RSSCT shall be designed using scaling equations derived based on proportional diffusivity assumptions. The methodology presented for Granular Activated Carbon shall be adapted for use with arsenic removal granular adsorptive media. The adsorptive media used for the RSSCT shall be a representative sample of unused virgin or regenerated media used in the package treatment plant. The RSSCT shall be designed to simulate the EBCT utilized in the package treatment plant.

Various sources for the feed water to be used for the RSSCT studies are possible. If pretreatment modules are included prior to adsorptive media as a part of the package

treatment plant, then this water may be sampled during steady-state operation of these treatment steps has been reached and used as influent to the RSSCT. An existing full-scale water treatment system may also be sampled if treatment steps and arsenic removal are representative of that achieved by the RSSCT. This would allow for the sampling of different water sources and qualities without necessitating transportation, set-up, and operation of the package plant to generate the RSSCT influent water. Alternatively, feed water may be sampled and batch treated under conditions that simulate treatment and arsenic removal by the package plant prior to adsorptive media treatment. In all cases, bench-scale filtration of the RSSCT influent water through a pre-rinsed 0.45- m filter is required. Depending on design and run time, the RSSCT volume of feed water shall be determined.

8.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include at a minimum arsenic concentration, pH, flow rates, and head loss (or pressure). Table 5 indicates the operational data monitoring frequencies. The FTO shall include acceptable values and ranges for all operational parameters monitored.

Water Quality Data Collection. During Adsorption Capacity Verification Testing utilizing either the package plant or the RSSCT, the adsorptive media feed water quality and treated water quality shall be characterized by analysis of the water quality parameters listed in Table 6. The sampling frequency described in Table 6 is intended to provide sufficient operational data and to effectively characterize the break-through profile of arsenic. Additional or more frequent analyses may be stipulated at the discretion of the FTO.

The exact sampling interval will depend on the length of verification testing. If the verification testing run time is specified by the FTO as a length of time (e.g., 60 days or 60 full-scale equivalent days) then the required number of samples shall be taken in evenly spaced intervals throughout the verification testing period. If verification testing run time is specified by the FTO as an effluent water quality criterion only, then a run time estimate¹ is needed to determine the appropriate sampling interval.

8.5 Evaluation Criteria and Minimum Reporting Requirements

8.5.1 Record of Arsenic Removal

Plot break-through curves (adsorptive media effluent concentrations versus bed volumes) for arsenic concentrations. Include plotted adsorptive media influent parameter concentrations versus bed volumes on the same plot. Calculate and tabulate average

¹All references to run times in the following discussion are full-scale run times. The discussion is applicable to both full-scale (package plant) and RSSCT studies, but run times need to be scaled down for application to RSSCT studies.

influent parameter concentrations. Compare arsenic removal with Manufacturer-specified removal goals. A sample form for reporting data is illustrated in Table 7.

8.5.2 Process Control

Record adsorptive media influent and effluent arsenic, pH, and pressure. Include adsorptive media influent average, standard deviation, and percent standard deviation for each analyte.

9.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

9.1 Introduction

During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of head loss gain. The volumetric flow rate through an adsorptive media vessel is a critical parameter, and must be monitored and documented. Adsorptive media performance is affected by the EBCT, which varies directly with the volumetric flow rate through the vessel.

9.2 Experimental Objectives

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to result in data that describe the operation of the equipment and data that can be used to develop cost estimates for operation of the equipment.

This task shall be performed in conjunction with System Integrity Verification Testing. This task shall also be performed in conjunction with Adsorption Capacity Verification Testing, when Adsorption Capacity Verification Testing is conducted using the package treatment plant. When Adsorption Capacity Verification Testing is conducted using RSSCTs, a summary description of the pretreatment applied to the water sampled for each RSSCT session shall be provided, including pretreatment steps, chemical dosages, flow rates, and any other relevant design and process information. In addition, design summary of the RSSCT shall also be provided, including, but not limited to particle size, scaling factor, column diameter, bed depth, volumetric flow rate, EBCT, velocity, minimum Reynolds number, porosity, dry bed density, and mass of adsorptive media utilized.

9.3 Work Plan

During each day of verification testing (both System Integrity Verification Testing and Adsorption Capacity Verification Testing), treatment equipment operating parameters for both pretreatment and adsorptive media shall be monitored and recorded on a routine basis. This shall include a complete description of pretreatment chemistry and all other applicable data.

Electrical energy consumed by the treatment equipment shall be measured, or as an alternative, the aggregate horsepower of all motors supplied with the equipment could be used to develop an estimate of the maximum power consumption during operation. Performance shall be evaluated to develop data on chemical dosages needed and on energy needed for operation of the process train being tested.

A complete description of the treatment process shall be given, with data on points of chemical addition, and volume and detention time of each process vessel at rated flow if applicable. Data on the adsorptive media vessel shall be provided and shall include the EBCT, depth, effective size, and uniformity coefficient of each layer of adsorptive media and support material. The type and source of adsorptive media used and the type of support material used shall be stated.

9.4 Schedule

Tables 1 and 2 presents the schedule for observing and recording package plant operation and performance data. The schedule applies to both System Integrity Verification Testing and Adsorption Capacity Verification Testing using the package plant. For Adsorption Capacity Verification Testing conducted using RSSCT, Tables 5 and 7 present the schedule for observing and recording RSSCT operating and performance data.

9.5 Evaluation Criteria

Where applicable, the data developed from this task shall be compared to Manufacturer's statements of performance capabilities. If no relevant statement of performance capability exists, results of operating conditions and performance data will be tabulated for inclusion in the Verification Report.

10.0 TASK 4: DATA MANAGEMENT

10.1 Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the adsorptive media and pretreatment equipment on a daily basis.

10.2 Experimental Objectives

The Objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the Field Testing Organization provides sufficient and reliable operational data to NSF for verification purposes.

10.3 Work Plan

The following protocol has been developed for data handling and data verification by the Field Testing Organization. Where possible, a Supervisory Control and Data Acquisition (SCADA)

system should be used for automatic entry of pilot-testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of adoptive media operation. At a minimum, backup of the computer databases to diskette should be performed on a monthly basis.

In the case when a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks. (Daily measurements shall be recorded on specially-prepared data log sheets as appropriate.) The laboratory notebook shall provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the Field Testing Organization at least once per week during testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Pilot operating logs shall include a description of the treatment equipment (description of test runs, names of visitors, description of any problems or events, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the print-out shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard-copies and corrected on the screen, and then a corrected version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (i.e., System Integrity Verification Testing runs or Adsorption Capacity Verification Testing runs) shall be assigned a run number which will then be permanently associated to the data from the experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA- accredited laboratories, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

11.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

11.1 Introduction

Quality assurance and quality control of the operation of the water treatment system, adsorptive media vessels, RSSCTs, and the measured water quality parameters shall be maintained during the verification testing Program.

11.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

11.3 Work Plan

Equipment flow rates and associated signals should be verified and verification recorded on a routine basis. A routine daily walk through during testing shall be established to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that any chemicals are being fed at the defined flow rate into a flowstream that is operating at the defined flow rate, such that the chemical concentrations are correct. In-line monitoring equipment such as flowmeters, etc. shall be calibrated to verify that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods or specified by the FTO.

It is extremely important that system flow rates are maintained at set values and monitored frequently. Doing so allows a constant and known EBCT to be maintained in the adsorptive media vessel or RSSCT. Adsorptive media performance is directly affected by the EBCT, which in turn is proportional to the volumetric flow rate through the contactor or RSSCT. Therefore, an important QA/QC objective shall be the maintenance of a constant volumetric flow rate through the adsorptive media vessel or RSSCT by frequent monitoring and documentation. Documentation shall include an average and standard deviation of recorded flow rates through the adsorptive media vessel or RSSCT.

11.3.1 Daily QA/QC Verifications:

- a) Chemical feed pump flow rates
- b) In-line pH, pressure and temperature (check calibration)
- c) Package plant adsorptive media vessel flow rate (verified volumetrically at least three times daily, approximately 4 hours apart)
- d) RSSCT column flow rate (verified volumetrically every four hours when staffed; at least three times daily)

11.3.2 Weekly QA/QC Verifications:

- a) In line flow meters/rotameters (clean equipment to remove any foulant buildup and verify flow rate volumetrically)
- b) In line turbidimeters (clean out reservoirs and recalibrate)
- c) Differential pressure transmitters (verify gauge readings and electrical signal using a dead weight calibration tester)
- d) Tubing (verify good condition of all tubing and connections, replace if necessary)

11.4 Analytical Methods

The analytical methods utilized in this study for on-site monitoring of adsorptive media influent and effluent water quality are described in the section below. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

11.4.1 Arsenic. Daily analyses for arsenic shall be performed on-site using Standard Method 3500-AsC (Silver Diethyldithiocarbamate Method). Weekly samples shall be performed in the lab for verification of on-site results using EPA Methods 200.7, 200.8, 200.9 or Standard Method 3113 B, 3114 B, 3120 B, 3500-B (Atomic Adsorption Spectrometric Method), or the Battelle Speciation Method (see Appendix A), if applicable. These analyses are the most critical for the entire ETV procedure. Minimum analytical turn around time is required to achieve optimum process control.

11.4.2 pH. Analyses for pH shall be performed on-site according to Standard Method 4500-H⁺ (Electrometric Method) or EPA Methods 150.1 and 150.2. A two-point calibration of the pH meter used in this study shall be performed once per day when the instruments are in use. Certified pH buffers in the expected range shall be used. The pH probes shall be stored in the appropriate solution defined in the instrument manual. If pH is adjusted in the process, pH readings are required before and after each pH adjustment.

11.4.3 Alkalinity. Analyses for alkalinity shall be performed on-site according to Standard Method 2320 B (Titration Method).

11.4.4 Fluoride. Analyses for fluoride shall be performed on-site according to Standard Method 4500-F⁻C (Ion-Selective Electrode Method) or EPA Method 300.

11.4.5 Chloride. Analyses for Chloride shall be performed in the lab according to Standard Method 4500-Cl⁻B (Argentometric Method) or 4500-Cl⁻C (Mercuric Nitrate Method) or EPA Method 300.

11.4.6 Sulfate. Analyses for sulfate shall be performed in the lab according to Standard Methods 4500 SO₄²⁻E (Turbidimetric Method), 4110 B, or EPA Methods 300 or 375.2.

11.4.7 Silica. Analyses for silica shall be performed in the lab according to Standard Method 4500 Si D (Molybdosilicate Method).

11.4.8 Aluminum. Analyses for aluminum shall be performed in the lab according to Standard Methods 3111D, 3113 B, 3500-A B (Atomic Absorption Method), or 3120 B, or EPA Methods 200.7, 200.8, or 200.9.

11.4.9 Sodium. Analyses for sodium shall be performed in the lab according to Standard Method 3500 Na B (Atomic Absorption Method).

11.4.10 Calcium. Analyses for calcium shall be performed on-site according to Standard Methods 3111 B or 3500 Ca D (EDTA Titrimetric Method), or EPA Method 200.7.

11.4.11 Hardness. Analyses for hardness shall be performed on-site according to Standard Method 2340 C (EDTA Titrimetric Method).

11.4.12 Magnesium. Analyses for magnesium shall be performed on-site according to Standard Method 3500 Mg E (Calculation Method) or EPA Method 200.7.

11.4.13 Iron. Analyses for iron shall be performed in the lab using Standard Methods 3500 - Fe B (Atomic Absorption Spectrometric Method), 3111 D, 3113 B, or 3120 B or EPA Methods 200.7, 200.8, 200.9.

11.4.14 Manganese. Analyses for manganese shall be performed in the lab using Standard Method 3500 Mn B (Atomic Absorption Spectrometric Method), 3111 D, 3113 B, or 3120 B or EPA Methods 200.7, 200.8, 200.9.

11.4.15 Turbidity. Turbidity analyses shall be performed according to Standard Method 2130 B or EPA Method 180.1 with either an in line or a bench top turbidimeter.

11.4.16 Temperature. Temperature shall be analyzed according to Standard Method 2550 B.

11.5 Chemical Samples Shipped Off-Site for Analyses

Samples must be analyzed immediately in the field for arsenic split samples shall be sent to the lab for verification of arsenic results.

Inorganic chemical samples, including arsenic, chloride, sulfate, silica, aluminum, sodium, iron, and manganese, shall be collected and preserved in accordance with Standard Method 3010 B, paying particular attention to the sources of contamination as outlined in Standard Method 3010 C. The samples should be refrigerated at approximately 2 to 8°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 2 to 8°C. Samples shall be processed for analysis by a state-certified or third party- or EPA- accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

11.6 Tests and Data Specific to Adsorptive Media Type Evaluated

The adsorptive media type used for testing shall be described by providing data on the adsorptive media type characteristics and tests listed in Table 7.

12.0 OPERATIONS AND MAINTENANCE

The following are recommendations for criteria for the evaluation of operations and maintenance (O&M) manuals for package plants employing adsorptive media for arsenic removal.

12.1 Operation

The manufacturer shall provide readily understood information on the required or recommended procedures related to the proper operation of the package plant equipment including, but not limited to, the following:

Monitoring of Preconditioning of Adsorptive Media:

- a) Utilize Manufacturer's Procedure which may vary depending upon adsorptive media selected
- b) Backwash Parameters (flow rate, time, backwash water turbidity, etc.)
- c) Pretreatment chemical application (chemical concentration, time, and flow rate)
- d) Volume of wastewater
- e) Wastewater disposal requirements (see Regeneration Wastewater Disposal below)

Monitoring Operation:

- a) Feed water arsenic concentration
- b) Feed water pH
- c) Feed water adjusted pH
- d) Feed water flow rate
- e) Feed water pressure
- f) Treated water arsenic concentration
- g) Treated water pH
- h) Treated water adjusted pH
- I) Treated water pressure
- j) Chemical feed rates
- k) Chemical consumption
- l) Electrical energy consumption
- m) Maintenance and operator labor requirements
- n) Spare parts requirements

Monitoring Regeneration of Adsorptive Media:

- a) Utilize manufacturer's procedure for regeneration which shall vary depending upon selected adsorptive media, equipment, and process variables
- b) Backwash parameters (flow rate, time, backwash water turbidity, etc.)
- c) Regeneration parameters (flow rate, time, regeneration chemical concentration and flow rate, effluent arsenic concentration, effluent pH , etc.)
- d) Neutralization (or transition to Arsenic Removal Treatment Mode) Parameters (flow rate, time, neutralization chemical concentration and flow rate, effluent arsenic concentration, effluent pH, adsorptive media depletion, etc.)
- e) Adsorptive media makeup requirement

Monitoring Regeneration Wastewater Disposal:

- a) Utilize manufacturer's procedure for processing, reclaiming, and/or disposing of regeneration wastewater, adsorptive media preconditioning wastewater, and waste solids, which shall vary depending upon selected adsorptive media, equipment, treatment chemicals and process variables
- b) pH adjustment parameters (flow rate, pH, time, pH adjustment chemical consumption, etc.)
- c) Flocculation/coagulation parameters (flow rate, time, flocculation/coagulation chemical consumption, etc.)
- d) Liquid/solid separation parameters (flow rate, time, etc.)
- e) Solids dewatering parameters (flow rate, time, sludge conditioning chemical consumption, dewatered sludge solids, content, toxicity of dewatered solids, etc.)
- f) Solids disposal parameters (volume, toxicity, permits, transportation of solids to disposal site, costs of transportation and disposal, etc.)
- g) Liquid disposal parameters (volume, toxicity, pH, permits, adjustment requirements, costs of disposal, etc.)

12.2 Maintenance

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- a) pumps
- b) valves
- c) all chemical feed and storage equipment
- d) all instruments

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- a) adsorptive media vessels
- b) feed lines
- c) manual valves

13.0 REFERENCES

Hathaway, S.W., and Rubel, F., Jr. 1987, "Removing Arsenic from Drinking Water," *Journal AWWA*, 79:8:161.

Sorg, T.J., and Logsdon, G.S. 1978. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2," *Journal AWWA*, 70:7:379.

Standard Methods for the Examination of Water and Wastewater. 1995. 19th edition. APHA, AWWA, and WEF, Washington, D.C.

USEPA. 1996a. ICR Manual for Bench- and Pilot-Scale Treatment Studies. Technical Support Division, Office of Ground Water and Drinking Water, Environmental Protection Agency.

Protocol for Arsenic Speciation, developed by Battelle for the EPA (see Appendix A).

TABLE 1
Schedule for observing and recording package plant operating and performance data

| Operational parameter | Action |
|---|--|
| Feed water and adsorptive media vessel volumetric flow rate | When staffed, check and record every four hours, adjust when >5% above or below target. Record before and after adjustment. |
| Adsorptive media vessel head loss | Record initial clean bed total head loss at start of run and record total head loss every four hours, when staffed. |
| Electric power | Record meter daily. |
| Chemicals used | Record name of chemical, supplier, commercial strength, dilution used for stock solution to be fed (if diluted) for all chemicals fed during treatment. |
| Chemical feed volume and dosage | Check and record every 4 hours. Refill as needed and note volumes and times of refill. |
| Hours operated per day | Record in log book at end of day or at beginning of first shift on the following work day. Any stoppage of flow to the adsorptive media vessel shall be recorded. Flow stoppage shall be accounted for by not including it in the cumulative operation time. |

TABLE 2

SYSTEM INTEGRITY VERIFICATION TEST CHEMICAL CONSUMPTION DATA REPORT^{a)}

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO. _____

ADSORPTIVE MEDIA _____

MANUFACTURER'S CHEMICAL CONSUMPTION CLAIM: _____ Chemical "A" _____ Gallons/1000gal
 _____ Gallons/1000gal
 Chemical "X" _____ Gallons/1000gal

| Event | Date/Time | Meter (gallons) | Meter ^{b)} (gallons) | Chemical "A" Day Tank (gallons) | Chemical "A" Dry Tank (gallons) | | | Chemical "X" ^{c)} Dry Tank (gallons) | Chemical "X" Dry Tank (gallons) |
|----------------------------|-----------|--------------------|----------------------------------|---------------------------------------|--|--|--|---|--|
| 1) Start Test | | | | | | | | | |
| 2) Fill Day Tank "A" | | | | | | | | | |
| 3) Fill Day Tank "X" | | | | | | | | | |
| 4) Fill Day Tank "A" | | | | | | | | | |
| (n-2) Fill Day Tank "X" | | | | | | | | | |
| (n-1) Fill Day Tank "A" | | | | | | | | | |
| (n) End Test | | | | | | | | | |

a) Data assembled on this report provides information which yields chemical consumption per thousand gallons of treated water. This in turn is to be converted to cost of each chemical per thousand gallons of treated water.

b) Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in minutes

c) "X" represents the total number of chemicals utilized, Therefore, if two chemicals are used, "X" becomes "B" etc.

TABLE 3
Required water quality analyses and minimum sample frequencies for
System Integrity Verification Testing

| Parameter | Frequency | Location | Standard Method ^a | EPA Method ^b |
|----------------------------------|------------------|----------------------------|--|--|
| Adsorptive Media Influent | | | | |
| Arsenic | Daily | On-Site & Lab ^c | 3113 B, 3114 B, 3120 B, 3500-AsC, 3500-AsB | 200.7/200.8/200.9, Battelle Speciation Method ^d |
| pH | 4 hour intervals | On-Site | 4500-H ⁺ B | 150.1/150.2 |
| Alkalinity | Daily | On-Site | 2320 B | |
| Fluoride | Daily | On-Site | 4500-F C | 300 |
| Chloride | Weekly | Lab | 4500-C ⁻ B, 4500-C ⁻ C | 300 |
| Sulfate | Weekly | Lab | 4110B, 4500-SO ₄ ²⁻ E | 300/375.2 |
| Silica | Daily | Lab | 4500-Si D | |
| Aluminum | Daily | Lab | 3111 D, 3113 B, 3500-A B, 3120 B | 200.7/200.8/200.9 |
| Sodium (optional) | Weekly | Lab | 3500-Na B | |
| Calcium | Weekly | On-Site | 3111 B, 3500-Ca D | 200.7 |
| Hardness | Weekly | On-Site | 2340 C | |
| Magnesium | Weekly | On-Site | 3500-Mg E | 200.7 |
| Iron | Weekly | Lab | 3111 D, 3113 B, 3500-Fe B, 3120 B | 200.7/200.8/200.9 |
| Manganese | Weekly | Lab | 3111 D, 3113 B, 3500-Mn B, 3120B | 200.7/200.8/200.9 |
| Turbidity | Daily | On-Site | 2130 B | 180.1 |
| Temperature | Daily | On-Site | 2550 B | |
| Adsorptive Media Effluent | | | | |
| Arsenic | Daily | On-Site & Lab ^c | 3113 B, 3114 B, 3120 B, 3500-AsC, 3500-AsB | 200.7/200.8/200.9, Battelle Speciation Method ^d |
| pH | 4 hour intervals | On-Site | 4500-H ⁺ B | 150.1/150.2 |
| Alkalinity | Daily | On-Site | 2320 B | |
| Fluoride | Daily | On-Site | 4500-F C | 300 |
| Chloride | Weekly | Lab | 4500-C ⁻ B, 4500-C ⁻ C | 300 |
| Sulfate | Weekly | Lab | 4110B, 4500-SO ₄ ²⁻ E | 300/375.2 |
| Silica | Daily | Lab | 4500-Si D | |
| Aluminum | Daily | Lab | 3111 D, 3113 B, 3500-A B, 3120 B | 200.7/200.8/200.9 |
| Sodium (optional) | Weekly | Lab | 3500-Na B | |
| Calcium | Weekly | On-Site | 3111 B, 3500-Ca D | 200.7 |
| Hardness | Weekly | On-Site | 2340 C | |
| Magnesium | Weekly | On-Site | 3500-Mg E | 200.7 |
| Iron | Weekly | Lab | 3111 D, 3113 B, 3500-Fe B, 3120 B | 200.7/200.8/200.9 |
| Manganese | Weekly | Lab | 3111 D, 3113 B, 3500-Mn B, 3120 B | 200.7/200.8/200.9 |
| Turbidity | Daily | On-Site | 2130 B | 180.1 |
| Temperature | Daily | On-Site | 2550 B | |

Notes:

^aStandard Methods Source: 19th Edition of Standard Methods for the Examination of Water and Wastewater, 1995, American Water Works Association.

^bEPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

^cLaboratory frequency to be weekly using Atomic Adsorption Spectrometric Method (3500- AsB) or Battelle Method.

^dSpeciation Method Developed by Battelle for EPA (see Appendix A).

TABLE 4
Tests and data specific to adsorptive media type evaluated

| Data | Parameter |
|--|--|
| Raw material used to make adsorptive media | |
| Method of manufacture: | Chemical processes Thermal processes Sizing / Screening methods Packaging methods |
| Preconditioning Procedure: | Wetting requirements Defining requirements Waste |
| Regeneration Procedure: | Backwash Chemical process Return to treatment mode Waste |
| Regeneration Results: | Adsorption capacity restored Adsorption media attrition Waste |
| Physical and chemical characteristics: | Percent voids Pore size Abrasion number Moisture (weight %) Particle size Sieve size, US sieve series Effective size Uniformity coefficient |

TABLE 5
Schedule for observing and recording RSSCT operating and performance data

| Operational parameter | Action |
|------------------------------|--|
| RSSCT flow rate | When staffed, check and record every four hours, adjust when >5% above or below target. Record before and after adjustment. |
| System pressure | When staffed, record every four hours |
| Hours operated per day | Record in log book at end of day or at beginning of first shift on the following work day. Any stoppage of flow to the RSSCT shall be recorded. Flow stoppage shall be accounted for by not including it in the cumulative operation time. |

TABLE 6
Required water quality analyses and minimum sample frequencies for
Adsorption Capacity Verification Testing

| Parameter | Frequency | Location | Standard Method ^a | EPA Method ^b |
|---|---|----------------------------|--|--|
| Adsorptive Media Influent^{c, d} | | | | |
| Arsenic | Daily & More Frequent Near Breakthrough | On-Site & Lab ^e | 3113 B, 3114 B, 3120 B, 3500-AsC, 3500-AsB | 200.7/200.8/200.9, Battelle Speciation Method ^f |
| pH | 4 hour intervals | On-Site | 4500-H ⁺ B | 150.1/150.2 |
| Alkalinity | Daily | On-Site | 2320 B | |
| Fluoride | Daily | On-Site | 4500-F C | 300 |
| Chloride | Weekly | Lab | 4500-C ⁻ B, 4500-C ⁻ C | 300 |
| Sulfate | Weekly | Lab | 4110B, 4500-SO ₄ ²⁻ E | 300/375.2 |
| Silica | Daily | Lab | 4500-Si D | |
| Aluminum | Daily | Lab | 3111 D, 3113 B, 3500-A B, 3120 B | 200.7/200.8/200.9 |
| Sodium (optional) | Weekly | Lab | 3500-Na B | |
| Calcium | Weekly | On-Site | 3111 B, 3500-Ca D | 200.7 |
| Hardness | Weekly | On-Site | 2340 C | |
| Magnesium | Weekly | On-Site | 3500-Mg E | |
| Iron | Weekly | Lab | 3111 D, 3113 B, 3500-Fe B, 3120 B | 200.7/200.8/200.9 |
| Manganese | Weekly | Lab | 3111 D, 3113 B, 3500-Mn B, 3120B | 200.7/200.8/200.9 |
| Turbidity | Daily | On-Site | 2130 B | 180.1 |
| Temperature | Daily | On-Site | 2550 B | |
| Adsorptive Media Effluent^{c, d} | | | | |
| Arsenic | Daily & More Frequent Near Breakthrough | On-Site & Lab ^e | 3113 B, 3114 B, 3120 B, 3500-AsC, 3500-AsB | 200.7/200.8/200.9, Battelle Speciation Method ^f |
| pH | 4 hour intervals | On-Site | 4500-H ⁺ B | 150.1/150.2 |
| Alkalinity | Daily | On-Site | 2320 B | |
| Fluoride | Daily | On-Site | 4500-F C | 300 |
| Chloride | Weekly | Lab | 4500-C ⁻ B, 4500-C ⁻ C | 300 |
| Sulfate | Weekly | Lab | 4110B, 4500-SO ₄ ²⁻ E | 300/375.2 |
| Silica | Daily | Lab | 4500-Si D | |
| Aluminum | Daily | Lab | 3111 D, 3113 B, 3500-A B, 3120 B | 200.7/200.8/200.9 |
| Sodium (optional) | Weekly | Lab | 3500-Na B | |
| Calcium | Weekly | On-Site | 3111 B, 3500-Ca D | 200.7 |
| Hardness | Weekly | On-Site | 2340 C | |
| Magnesium | Weekly | On-Site | 3500-Mg E | 200.7 |
| Iron | Weekly | Lab | 3111 D, 3113 B, 3500-Fe B, 3120 B | 200.7/200.8/200.9 |
| Manganese | Weekly | Lab | 3111 D, 3113 B, 3500-Mn B, 3120 B | 200.7/200.8/200.9 |
| Turbidity | Daily | On-Site | 2130 B | 180.1 |
| Temperature | Daily | On-Site | 2550 B | |

Notes:

^aStandard Methods Source: 19th Edition of Standard Methods for the Examination of Water and Wastewater, 1995, American Water Works Association.

^bEPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

^cInfluent sampling shall occur at approximately the same time as effluent sampling for each parameter during package plant operation.

^dWhen RSSCT is employed using single batch of feed water, only one test is required except for pH.

^eLaboratory frequency to be weekly using Atomic Adsorption Spectrometric Method (3500- AsB) or Battelle Method.

^fSpeciation Method Developed by Battelle for EPA (see Appendix A).

TABLE 7

ADSORPTION CAPACITY VERIFICATION DATA REPORT

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO _____
 ADSORPTIVE MEDIA _____ RATED CAPACITY _____ mg/L/FT³

| Date/Time | Minutes ^{a)} | Flow Rate (gpm) | Meter (gallons) | Meter ^{b)} (gallons) | Pressure ^{c)} (psig) | Feed Arsenic (mg/L) | Treated Arsenic (mg/L) | Arsenic Removed ^{d)} (mg) | Cumulative Arsenic Removed (mg) |
|--------------|-----------------------|--------------------|--------------------|----------------------------------|----------------------------------|---------------------------|------------------------------|--|---------------------------------------|
| <u>Start</u> | | | | | | | | | |
| 1) | | | | | | | | | |
| 2) | | | | | | | | | |
| 3) | | | | | | | | | |
| 4) | | | | | | | | | |
| n-3) | | | | | | | | | |
| n-2) | | | | | | | | | |
| n-1) | | | | | | | | | |
| <u>End</u> | | | | | | | | | |
| n) | | | | | | | | | |

a) Time (n) - Time (n-1) in minutes

b) Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in gallons

c) Influent pressure - effluent pressure (gauge reading differential pressure)

d)
$$\frac{[\text{Feed Arsenic (n)} - \text{Treated Arsenic (n)}] + [\text{Feed Arsenic (n-1)} - \text{Treated Arsenic (n-1)}]}{(2)} \times [\text{meter (n)}] \text{ in mg}$$